DYNAMICS OF ASPHALTENES SOLUTIONS IN TOLUENE STUDIED BY MEANS OF THEIR ADSORPTIONS ON GLASS SURFACES

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Using conventional VPO measurements in toluene and thermal lens spectroscopy (a laser technique) to measure the adsorption of asphaltenes on a glass surface from toluene solutions, the dynamics of Hamaca asphaltene solutions have been studied. The results described below are consistent with two dynamic events occuring at very different rates. In the first one the adsorbed asphaltenes were measured directly by the above laser method. When the signal corresponding to this adsorbed sample was plotted against time (solution concentration: 4000 mgl^{-1}) a maximum, near 125 min was observed. A much lower and steady value for the signal was observed after 300 min. A similar experiment was performed with resins and a low and constant signal was observed in this case. The second event was the slow increase of average molecular weight where the number average molecular weight M_n increased, during a period of two days, from 4230 to 17420 in toluene.

Experimental.
Two Hamaca asphaltene samples were examined. Sample A_1 were asphaltenes precipitated from extraheavy (8° API) Hamaca crude oil by adding 40 volumes of n-heptane to a 1:1 mixture of crude and toluene as described earlier. This sample contains about 80% asphaltenes and 20% of resins. Sample A_2 was a resin-free asphaltene obtained by washing the above A_1 sample with boiling n-heptane in a soxhlet apparatus during a period of three days.

M_n determinations.
These were measured in toluene at 50°C in a concentration range from 1 to 5 g l^{-1} as described earlier[1]. Results are shown on Table 1 for Hamaca and for similar samples of asphaltenes obtained from another extraheavy crude oil (Cerro Negro) wich are included for companson. As shown in this table, the M_n for the A_1 samples could be averaged whereas the values for A_2 increase steadily with time. Due to limitations of the VPO technique it was imposible to measure M_n values higher than those shown on Table 1.

Hamaca Asphaltenes,							
	Time	(hours)					
	0	24	48	72	96	144	216
A_1[a]	2760	2820	2850	3350	2380	3010	2230
A_2	4230	4330	17420	b	b	b	b
a:average 2770±375							
Cerro Negro Asphaltenes							
A_1[c]	2570	3220	2880	2570	-	3500	3100
A_2	5350	5470	10720	15170	b	b	b
b: M_n too high to be measured by this method							
c:average 2970±370							

Table 1. M_n values vs time for asphaltene samples.

Thermal Lens Spectroscopy.
For thermal lens measurements we have used a home made thermal lens spectrometer with a collinear dual-beam configuration (see Figure 1).
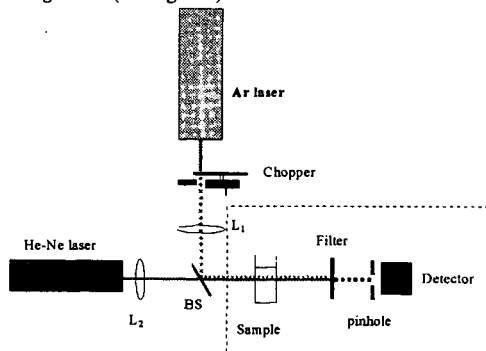

Figure 1. Experimental set-up for thermal lens spectroscopy.

A Coherent Innova 300 argon ion laser (250 mW, 488 nm3 was used as a pump or excitation beam whose amplitud was modulated by a chopper and was focused onto the sample with a lens L_1 (200 mm focal lenght). In the present case, the sample cell was the glass slide described below. A 5 mW He-Ne laser (632.8 nm) was used as probe beam and focused with lens L_2 (200 mm focal lenght). The probe beam focus is placed 6 cm before the sample cell. A 50% beam splitter (BS) was used in order to direct collineary the exitation and probe beam through" the sample cell. The signal was obtained by sampling the intensity at the center of the probe beam with a precision pinhole and a silicon photodiode. The detector-pinhole system was mounted on a XYZ translator in order to localize the laser beam center.

Adsorption Measurements.
Toluene solutions of the above A_2 Hamaca samples were prepared as required using an ultrasound apparatus to dissolve the asphaltenes as fast as possible. For diluted solutions (< 1 gl^{-1}) this required less than a minute whereas for the more concentrated the solutions were sonicated for 15 minutes to ensure completed dissolution. Glass slides (4 cm x 1 cm), used as adsorption surfaces, were dipped in the above solutions and stored in stoppered compartments. After the appropriate times, these were withdrawn, dried and analyzed using the the above thermal lens spectroscopy. Signal averages were obtained by impinging the beams on differents spots on the glass surface. Two types of experiments were performed: In the first, we monitored the signal against the time for a 4 gl^{-1} solution of asphaltene in toluene. The results are plotted in Figure 2. In the second type, toluene solutions of different concentrations were prepared, the glass slides were dipped in and measurements were recorded after 78 hours. The results are plotted on Figure 3.

Disscusion.
a. Time dependent experiments.
The results shown on Figure 2, could be analyzed in terms of the following considerations: During the first stages of the dissolution process the asphaltenes are present in solution as large particles formed by the association of aggregates.
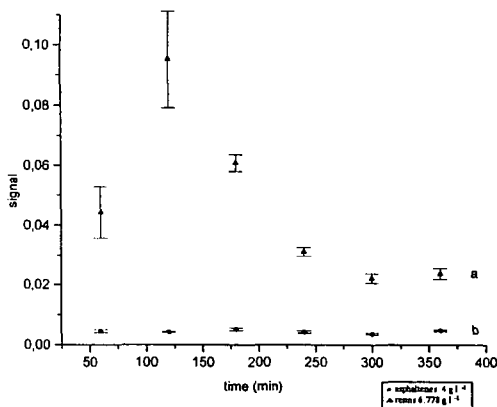

Figure 2.   Adsorption of A_2 Type asphaltenes (a) and resins (b) on a glass surface as a function of time.

To simplify the arguments these could be represented as A_n where each A component is an asphaltene aggregate formed by a range of molecular weight compounds from large (A_L) to small (A_s) molecular weight components. The A_n and A macrostructures and composition would depend on the precipitation conditions used to obtain the samples (A_1 type) as well as on any further treatment employed to purify the sample (A_2 type). For instance, in macrostructure A the large components A_L, formed by aromatic structures bonded through aliphatic chains in a way similar to that suggested by Strausz et al[2] would be placed at the perifery of A enclosing smaller molecular weight components. In any case we suggest that during the first stages of the adsorption process, the predominant species present in solution would be the A_n whose adsorption would account for the increase in the signal S(t) in Figure 2. After a while, dissociation of A_n in their A components will set in leading to the observed decrease in S(t) since in principle adsorption of a lower molecular weight species (A) leads to a decrease in S(t). As shown in Figure 2, this process occurs during the first 300 minutes of measurements.

To account for the behaviour of M_n measured for the A_1 and A_2 samples (see Table 1) we suggest that due to entropic factors, the solvent will enter the A macrostructure breaking internal weak bonds between their components and releasing some of them. Then, the system will move to an equilibrium state consistent with the prevailing conditions of solvent, concentration and temperature. The above dynamic behaviour could be summarized by noting that both A_n and A macrostructures, as they are in samples A_1 and A_2 are not equilibrium macrostructures in toluene. For instance, the increase in M_n with time, for samples A_2 is likely due to the removal or resins from asphaltene sites active for molecular interaction when the sample is dissolved in toluene.

b. Concentration dependent experiments.

The adsorption isotherms of asphaltenes on inorganic surfaces, using conventional UV absorption spectroscopy, have been studied in our labs earlier[3]. However, due to experimental limitations inherent to this technique which leads to errors comparable or larger than the amount of sample adsorbed, the measumerents have to be made at very low concentrations, usually below 200 mgl^{-1}. Figure 3 show clearly that use of the above thermal lens technique leads to fairly good results at low and high concentrations, due to the direct measurement of the amount adsorbed and to the high sensitivity of the laser beam. The adsorption isotherm shown in Figure 3 for Hamaca (A_2 sample) is consistent with a Langmiur type adsorption at low concentration. As discussed elsewhere[3], the "jump" near 1000 mgl^{-1} is probably due to the adsorption of aggregates formed after the cmc corresponding to this sample.
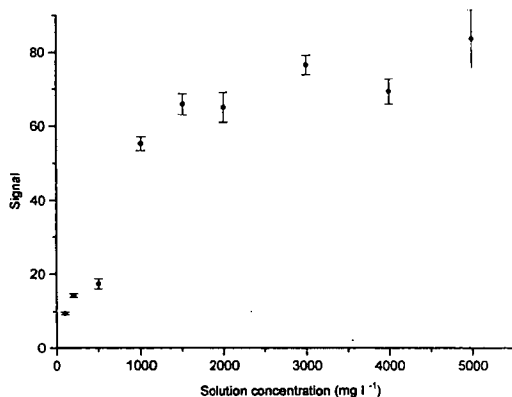

Figure 3.   Adsortion isotherm of Hamaca asphaltenes (A_2 Type). Solvent: Toluene. Temperature: 25°C.

References.

1. Acevedo, S., Mendez, B., Rojas, A., Layrissc, I, and Rivas, H., Fuel, 64, 1741 (1985).

2. Strausz, O. P., Mojelsky, T. W., and Lown, R.M., Fuel, 71, 1355 (1992).

3. Acevedo, S., Ranaudo, M. A., Escobar, G., Gutierrez, L., and Ortega, P., Fuel, 74, 595 (1995).